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(54) Title: CELLS

(57) Abstract: There is described a fuel cell or electrolytic cell comprising an ion-conductive polymeric material which includes a first repeat unit of formula (I): - (O-Ph¹-CO-Ph¹-O-Ph¹-CO-Ph¹) -, and a second repeat unit of formula (II): - (O-Ph²-O-Ph³-CO-Ph⁴) -, or of formula (III): (O-Ph²-O-Ph³-SO₂-Ph⁴) -; wherein Ph¹, Ph², Ph³ and Ph⁴ independently represent phenyl moieties and wherein said second repeat unit is provided with ion-exchange sites. The polymeric material may include a third repeat unit which is amorphous.



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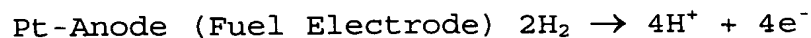
Cells

This invention relates to cells and particularly, although not exclusively, relates to a fuel cell per se and an electrolytic cell per se. Especially preferred
5 embodiments relate to fuel cells.

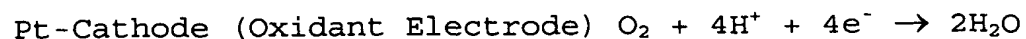
One type of polymer electrolyte membrane fuel cell (PEMFC), shown schematically in Figure 1 of the
10 accompanying diagrammatic drawings, may comprise a thin sheet 2 of a hydrogen-ion conducting Polymer Electrolyte Membrane (PEM) sandwiched on both sides by a layer 4 of platinum catalyst and an electrode 6. The layers 2, 4, 6 make up a Membrane Electrode Assembly (MEA) of less than
15 1mm thickness.

In a PEMFC, hydrogen is introduced at the anode (fuel electrode) which results in the following electrochemical reaction:

20



The hydrogen ions migrate through the conducting PEM to the cathode. Simultaneously, an oxidant is introduced at
25 the cathode (oxidant electrode) where the following electrochemical reaction takes place:



30 Thus, electrons and protons are consumed to produce water and heat. Connecting the two electrodes through an

external circuit causes an electrical current to flow in the circuit and withdraw electrical power from the cell.

Preferred ion-conducting polymeric materials for use
5 as components of polymer electrolyte membranes in fuel
cells have high conductivity (low EW, or high ion-exchange
capacities) and optimum water uptake for good conductivity
and mechanical properties. To increase conductivity of a
polymeric material it may be provided with an increased
10 concentration of ion-exchange sites, for example
sulphonate groups. However, the greater the ionic
character of the polymeric material, the more soluble the
polymeric material is likely to be in water and/or the
water absorbance of the polymeric material may increase
15 too much. Since water at high temperature is generated as
a bi-product of the electrochemical reaction in a fuel
cell, the greater the solubility and/or water uptake of
the polymeric material, the greater the rate of
disintegration of the polymeric material and the lower the
20 useful lifetime of the cell.

US 5362836 (Hoechst) discloses, in the specific
examples, only the preparation of sulphonated
polyetheretherketone and sulphonated
25 polyetheretheretherketoneketone homopolymers. The
sulphonation conditions are varied to vary the level of
sulphonation and, therefore, properties of the polymers.
No values are given for the boiling water uptake of the
sulphonated polymers prepared. Furthermore, it should be
30 appreciated that it is difficult to precisely control
and/or reproduce the level of sulphonation and,
consequently, the properties of the ion-conductive
polymers and that this could lead to difficulties in

producing polymers of the type described for commercial use.

US 5438082 (Hoechst), US 5561202 (Hoechst) and US
5 5741408 (Hoechst) address the problem of preparing polymer
electrolyte membranes comprising sulphonated aromatic
polyetherketones which have increased stability. The
solution described involves the preparation of sulphonated
aromatic polyetherketone polymers, conversion of
10 sulphonate groups of the polymers to sulphonyl chloride
groups, treatment of the sulphonyl chloride groups with an
amine containing at least one cross-linkable substituent
to produce a sulphonamide group, hydrolysing unreacted
sulphonyl chloride groups, isolating the resultant
15 aromatic sulphonamide and dissolving it in an organic
solvent, converting the solution into a film and then
cross-linking the crosslinkable substituents in the film.

US 5795496 (California Institute of Technology)
20 describes polymer materials for electrolyte membranes in
fuel cells which are intended to have high proton
conductivity and be stable at high temperature. Preferred
materials are sulphonated polyetheretherketone or
sulphonated polyethersulphone. These materials are
25 modified, by controlled cross-linking of sulphonate
groups, to provide materials with asymmetric permeability
properties.

US 5834566 (Hoechst) addresses the problem of
30 providing films of improved properties for electrochemical
uses. The solution described is the provision of
homogenous polymer alloys, for example of sulphonated
polyetherketone and non-sulphonated polyethersulphone, in

combination with a hydrophilic polymer, for example of polyvinylpyrrolidone or polyglycol dimethylether.

WO96/29360 (Hoechst) addresses the problem of
5 increasing the level of sulphonation of polyetherketones by providing a method of sulphonating -O-phenyl-CO- units thereof. The specific examples disclose the application of the method to polyetheretherketone and polyetheretherketoneketone homopolymers.

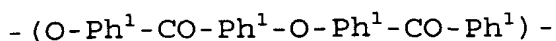
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It will be appreciated from the above that there have been many proposed solutions to the problem of providing suitable ion-conductive polymeric materials for use in fuel cells and that some of the proposals are complex, for
15 example by including multi-step processes, potentially expensive and/or difficult to reproduce on a commercial scale.

It is an object of the present invention to provide an
20 ion-conductive polymeric material for a fuel cell or electrolytic cell which may be improved compared to prior art proposals.

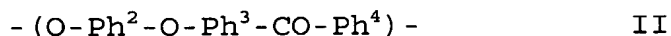
The present invention is based on the discovery of
25 certain copolymers which are surprisingly advantageously adapted for use in fuel cells or electrolytic cells.

According to a first aspect of the invention, there is provided a fuel cell or an electrolytic cell comprising an
30 ion-conductive polymeric material which includes a first repeat unit of formula



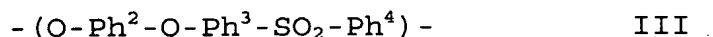
I

and a second repeat unit of formula



5

or of formula



10 wherein Ph^1 , Ph^2 , Ph^3 and Ph^4 independently represent phenyl moieties and wherein said second repeat unit is provided with ion-exchange sites.

Surprisingly, it is found that ion-conductive
15 polymeric materials of the type described have boiling water uptakes, when used in fuel cells and/or electrolytic cells, which are much lower than expected and, more particularly, much lower than found for ion-conductive polymeric materials of similar equivalent weights (EW)
20 comprising a single ion-conducting homopolymer of formula I, II or III.

Unless otherwise stated in this specification, a phenyl moiety may have 1,4- or 1,3-, especially 1,4-, linkages to
25 moieties to which it is bonded.

Said ion-conductive polymeric material is preferably crystalline.

30 The existence and/or extent of crystallinity in a polymer is preferably measured by wide angle X-ray diffraction, for example as described by Blundell and Osborn (Polymer 24, 953, 1983). Alternatively,

Differential Scanning Calorimetry (DSC) could be used to assess crystallinity. The level of crystallinity in said ion-conductive polymeric material may be at least 0.5% suitably at least 1%, preferably at least 5%, more preferably at least 10%, especially at least 15% weight fraction, suitably when measured as described by Blundell and Osborn. In some cases, the level of crystallinity, when measured as described may be at least 20% weight fraction. The level of crystallinity in said first polymeric material may be less than 30% weight fraction, preferably less than 25% weight fraction.

Said ion-conductive polymeric material suitably includes a repeat unit which is crystalline and a repeat unit which is amorphous. Said first repeat unit is preferably crystalline. Preferably, less than 1 mole% of groups Ph^1 in said polymeric material are sulphonated and/or otherwise functionalised. Preferably, said first repeat unit comprises unsubstituted phenyl groups Ph^1 with said groups Ph^1 suitably having 1,4-linkages to the -O- and -CO- groups to which they are bonded. Preferably, substantially no groups Ph^1 are substituted in said ion-conductive polymeric material.

Said second repeat unit preferably includes ion-exchange sites. Suitably, to provide said ion-exchange sites, said second repeat unit is sulphonated, phosphorylated, carboxylated, quaternary-aminoalkylated or chloromethylated, and optionally further modified to yield $-\text{CH}_2\text{PO}_3\text{H}_2$, $-\text{CH}_2\text{NR}_3^{20+}$ where R^{20} is an alkyl, or $-\text{CH}_2\text{NAr}_3^{x+}$ where Ar^x is an aromatic (arene), or provided with $-\text{OSO}_3\text{H}$ or $-\text{OPO}_3\text{H}_2$ cationic exchange sites as described in WO95/08581.

Preferably, said second repeat unit is sulphonated. Preferably, the only ion-exchange sites of said second repeat unit are sites which are sulphonated.

5 References to sulphonation include a reference to substitution with a group $-\text{SO}_3\text{M}$ wherein M stands for one or more elements selected with due consideration to ionic valencies from the following group: H, NR_4^{y+} , in which R^y stands for H, $\text{C}_1\text{-C}_4$ alkyl, or an alkali or alkaline earth
10 metal or a metal of sub-group 8, preferably H, NR_4^+ , Na, K, Ca, Mg, Fe, and Pt. Preferably M represents H.

Preferably less than 1 mole% of groups Ph^3 in said second unit are sulphonated and/or otherwise
15 functionalised. Preferably less than 1 mole% of groups Ph^4 are sulphonated and/or otherwise functionalised. Preferably, substantially no groups Ph^3 are substituted. Preferably, substantially no groups Ph^4 are substituted. Preferably Ph^3 represents an unsubstituted phenyl group,
20 suitably having 1,4-linkages to the $-\text{O}-$ and $-\text{CO}-$ (or $-\text{SO}_2-$) groups to which it is bonded. Preferably, Ph^4 represents an unsubstituted phenyl groups, suitably having 1,4-linkages to the $-\text{O}-$ and $-\text{CO}-$ (or $-\text{SO}_2-$) groups to which it is bonded.

25

Suitably, greater than 70 mole%, preferably greater than 80 mole%, more preferably greater than 90 mole% of groups Ph^2 in said second unit are provided with ion-exchange sites, especially sulphonate groups. Groups Ph^2
30 may be provided with a single ion-exchange site - i.e. they are preferably only monosulphonated.

In general terms, phenyl groups of -O-phenyl-O-moieties (e.g. Ph²) may be provided with ion-exchange sites, for example sulphonated, readily, e.g. using the relatively mild method described in Examples 2a to 2c hereinafter, (i.e. using a sulphuric acid concentration of less than 98.5% and avoiding the use of oleum) so that up to 100 mole% of the phenyl groups are provided with ion-exchange sites (e.g. sulphonated). However, the phenyl groups of -O-phenyl-CO- moieties and of -O-phenyl-SO₂- moieties (e.g. Ph¹, Ph³ and Ph⁴) are relatively difficult to provide with ion-exchange sites (and, therefore, are not provided with ion-exchange sites) due to deactivation of the phenyl moieties by -CO- or -SO₂- groups.

Preferably, Ph² represents a phenyl group provided with an ion-exchange site wherein the phenyl group has 1,4-linkages to the -O- groups to which it is bonded.

Said second unit suitably is, by virtue of it being provided with ion-exchange sites, amorphous.

Said ion-conductive polymeric material could include repeat units of formula II and III, each of which is provided with ion-exchange sites. Preferably, however, it includes either unit II or unit III (and not both).

An especially preferred second repeat unit is of formula II. Thus, said second repeat unit is preferably an -ether-(monosulphonated)phenyl-ether-(unsubstituted)phenyl-carbonyl-(unsubstituted)phenyl-unit.

Suitably, "a" represents the mole% of units of formula I in said ion-conductive polymeric material, and "b" represents the sum of the mole% of units of formulae II and III in said polymeric material. Suitably, the ratio of "a" to "b" in said polymeric material is less than 4, preferably less than 3, more preferably less than 2, especially less than 1. The ratio of "a" to "b" may be at least 0.15, suitably at least 0.25, preferably at least 0.3, more preferably at least 0.4, especially at least 0.5.

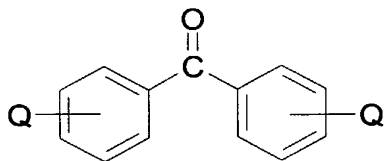
Said ion-conductive polymeric material may be a random or block copolymer comprising units I, II and/or III. Preferably, said ion-conductive polymeric material is a random copolymer.

Said ion-conductive polymeric material may include a third repeat unit which is suitably different from units I, II and III. Said third unit is preferably amorphous. Said third unit is preferably not crystalline or crystallisable. Said third unit is preferably not provided with ion-exchange sites. Said optional third unit preferably includes phenyl groups linked by -CO-, -SO₂-, -O- and/or -S- provided said third unit is more difficult to provide with ion-exchange sites (e.g. sulphonate) compared to the ease with which said second unit (prior to its functionalisation as described) can be provided with ion-exchange sites (e.g. sulphonated) and provided said third unit is amorphous. To this end, said third unit suitably includes a means to render it amorphous (hereinafter "said amorphous means") and/or not crystallisable with polyetherketone units. Said third unit may include a moiety of formula -Q-Z-Q- wherein Z

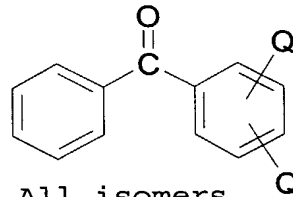
represents an aromatic group containing moiety and Q is -O- or -S-, wherein said unit of formula -Q-Z-Q- is not symmetrical about an imaginary line which passes through the two -Q- moieties provided, however, that said unit is
5 not derived from dihydroxybenzophenone substituted by groups Q at the 4- and 4'- positions (since such a benzophenone acts in the manner of a symmetrical moiety by virtue of the carbonyl group being substantially similar to an ether group thereby allowing the carbonyl group to
10 be interchanged with an ether group in a polyaryletherketone crystal lattice).

Examples of units of formula -Q-Z-Q- (especially where Q is -O-) are as follows:

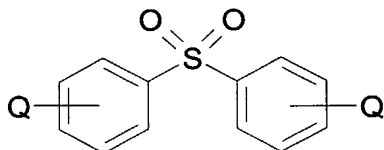
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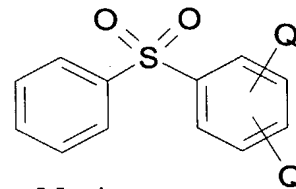
All isomers but not 4,4'-isomer



All isomers



All isomers
- includes 4,4'-isomer

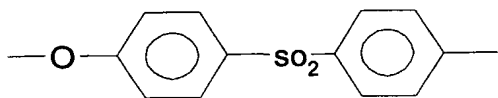


All isomers

Said third repeat unit preferably includes at least
5 one of the following: a sulphone moiety in the polymer backbone; a 1,3-disubstituted phenyl moiety in the polymer backbone; or a functional group pendent from a phenyl moiety in the polymer backbone.

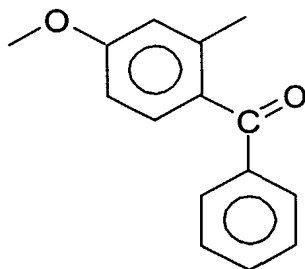
10 Preferred optional third units are of general formula
-O-Ph-(SO₂-Ph)_{n1}-(CO-Ph)_{n2}-[AMOR]- IV

wherein Ph represents a phenyl group, n1 is 0, 1 or 2,
n2 is 0, 1 or 2 and AMOR represents an amorphous unit, for
15 example of formulae:

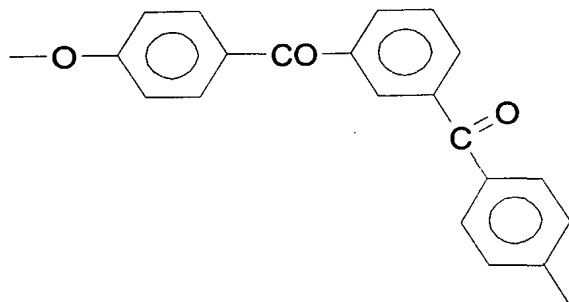


V

5



VI



10

VII

The phenyl groups of the third unit of formula IV may be
 15 1,3- or 1,4-substituted by the groups shown. Preferably,
 they are 1,4-substituted.

Preferred third units are: -ether-phenyl-ketone-
 phenyl-[AMOR]- (i.e. $n_1=0$, $n_2=1$), -ether-phenyl-sulphone-
 20 phenyl-[AMOR]- (i.e. $n_1=1$, $n_2=0$), where [AMOR] represents
 V, VI or VII.

Preferably, "c" represents the mole% of said third units in said ion-conductive polymeric material and "a" and "b" are as described above. The ratio of "c" to the sum of "a" and "b" is suitably less than 0.25, preferably less than 0.2, more preferably less than 0.15, especially less than 0.125.

Suitably, "c" is 30 mole% or less, preferably 20 mole% or less, more preferably 15 mole% or less, especially 10 mole% or less. Suitably "a" is at least 30 mole%, preferably at least 40 mole%, more preferably at least 45 mole%, especially at least 50 mole%. Suitably, "a" is 85 mole% or less. Suitably, "b" is at least 70 mole% or less, preferably 60 mole% or less, more preferably 55 mole% or less, especially 50 mole% or less.

The equivalent weight (EW) of said ion-conductive polymeric material is preferably less than 850 g/mol, more preferably less than 800g/mol, especially less than 750 g/mol. The EW may be greater than 300, 400 or 500 g/mol.

The boiling water uptake of ion-conductive polymeric material measured as described in Example 4 is suitably less than 350%, preferably less than 300%, more preferably less than 250%.

The glass transition temperature (T_g) of said ion-conductive polymeric material may be at least 144°C, suitably at least 150°C, preferably at least 154°C, more preferably at least 160°C, especially at least 164°C. In some cases, the T_g may be at least 170°C, or at least 190°C or greater than 250°C or even 300°C.

Said ion-conductive polymeric material may have an inherent viscosity (IV) of at least 0.1, suitably at least 0.3, preferably at least 0.4, more preferably at least 0.6, especially at least 0.7 (which corresponds to a reduced viscosity (RV) of least 0.8) wherein RV is measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84gcm⁻³, said solution containing 1g of polymer per 100cm⁻³ of solution. IV is measured at 25°C on a solution of polymer in concentrated sulphuric acid of density 1.84gcm⁻³, said solution containing 0.1g of polymer per 100cm³ of solution. The measurements of both RV and IV both suitably employ a viscometer having a solvent flow time of approximately 2 minutes.

15

The main peak of the melting endotherm (T_m) for said ion-conductive polymeric material may be at least 300°C.

Said semi-crystalline polymer may comprise a film, suitably having a thickness of less than 1mm, preferably less than 0.5mm, more preferably less than 0.1mm, especially less than 0.05mm. The film may have a thickness of at least 5µm.

The invention of the first aspect preferably relates to a fuel cell. Said ion-conductive polymeric material preferably comprises a part of an ion-conducting membrane of said fuel cell. Said ion-conducting membrane is preferably substantially non-permeable. Said ion-conductive membrane may consist essentially of said ion-conductive polymeric material. In this case, said membrane comprises a unitary material which may define a PEM of the fuel cell. A catalyst material may be

associated with the polymeric material, suitably on opposite sides thereof. Alternatively, said ion-conductive polymeric material may be part of a composite ion-conducting membrane. Said composite ion-conducting
5 membrane may comprise said ion-conductive polymeric material blended with other ion-conducting or non-ion-conducting amorphous or crystalline polymeric materials. Alternatively, said ion-conductive polymeric material may be associated with a composite membrane material. For
10 example, said ion-conductive polymeric material in the form of an unsupported conductive polymer film can be contacted with, for example laminated to, a said composite membrane material. Alternatively, one of either said composite membrane material or said ion-conductive polymeric material
15 may be impregnated with the other one of either said composite membrane material or said ion-conductive polymeric material.

Said composite membrane material may be a support
20 material for supporting said ion-conductive polymeric material. In this case, said composite membrane material preferably is stronger and/or has a lower water absorbance compared to said ion-conductive polymeric material.

25 Alternatively, said ion-conductive polymeric material may be a support for the composite membrane material.

The invention extends to a plurality of fuel cells as described according to the first aspect. The fuel cells
30 are preferably substantially identical to one another and are preferably provided in a stack in series. Greater than 50 or even greater than 100 of said fuel cells may be provided in a said stack.

Said plurality of fuel cells may together include more than 0.1m^2 , suitably more than 0.5m^2 , preferably more than 1m^2 , more preferably more than 5m^2 of said ion-conductive
5 polymeric material. The amount of said ion-conductive polymeric material may be less than 100m^2 .

According to a second aspect of the invention, there is provided a polymer electrolyte membrane for a fuel cell
10 or electrolytic cell (especially for a fuel cell), the membrane comprising an ion-conductive polymeric material as described according to said first aspect.

Said polymer electrolyte membrane (PEM) may have a
15 dimension in a first direction of at least 1cm. The dimension of the PEM in a second direction, perpendicular to the first direction, may also be at least 1cm. Where the PEM is circular, the diameter may be at least 1cm. In some cases, for example for vehicle applications, the
20 dimension(s) in the first and/or second direction(s) may be at least 10cm or at least 20cm. The dimension(s) in the first and second direction(s) is/are suitably less than 100cm, preferably less than 50cm, more preferably less than 35cm.

25

Said PEM may comprise one or more layers wherein, suitably, at least one layer comprises a film of said semi-crystalline polymer. Said membrane may have a thickness of at least $5\mu\text{m}$ and, suitably, less than 1mm,
30 preferably less than 0.5mm, more preferably less than 0.1mm, especially less than 0.05mm.

According to a third aspect of the invention, there is provided a membrane electrode assembly for a fuel cell which comprises an ion-conductive polymeric material according to said first aspect associated with a catalyst material. Catalyst material is preferably associated with opposing sides of the ion-conducting polymeric material.

According to a fourth aspect of the present invention, there is provided a method of making a fuel cell or electrolytic cell, the method comprising incorporating an ion-conductive polymeric material according to said first aspect into said fuel cell or electrolytic cell.

According to a fifth aspect of the invention, there is provided a method of making a fuel cell or electrolytic cell, the method comprising incorporating, into the fuel cell or electrolytic cell, an ion-conductive polymeric material prepared by:

(A) polycondensing 4,4'-dihydroxybenzophenone (DHB), 4,4'-difluorobenzophenone (BDF) and hydroquinone (HQ);

(B) treating the polymeric material formed with a means for providing said ion-exchange sites.

The polycondensation reaction may, optionally, be carried out in the presence of other monomers. Examples include 4,4'-dichlorodiphenylsulphone (DCDPS) and/or 4,4'-difluorodiphenylsulphone (DFDPS).

The polycondensation reaction described for making an ion-conductive polymeric material according to the first aspect and/or using the method described in the fifth

aspect is suitably carried out in the presence of a base, especially an alkali metal carbonate or bicarbonate or a mixture of such bases. Preferred bases for use in the reaction include sodium carbonate and potassium carbonate
5 and mixtures of these.

The identity and/or properties of the polymers prepared in a polycondensation reaction described may be varied according to the reaction profile, the identity of
10 the base used, the temperature of the polymerisation, the solvent(s) used and the time of the polymerisation. Also, the molecular weight of a polymer prepared may be controlled by using an excess of halogen or hydroxy reactants, the excess being, for example, in the range 0.1
15 to 5.0 mole%

Said means for providing said ion-exchange sites preferably involves sulphonating the polymeric material. Sulphonation conditions are preferably selected wherein
20 Ph^2 phenyl groups can be sulphonated but relatively deactivated Ph^1 , Ph^3 and Ph^4 phenyl groups generally cannot be sulphonated. To this end, sulphonation may be carried out in concentrated sulphuric acid (suitably at least 96% w/w, preferably at least 97%w/w, more preferably at least
25 98%w/w; and preferably less than 98.5%w/w) at an elevated temperature. For example, dried polymer may be contacted with sulphuric acid and heated with stirring at a temperature of greater than 40°C, preferably greater than 55°C, for at least one hour, preferably at least two hours,
30 more preferably at least five hours especially at least ten hours. The desired product may be caused to precipitate, suitably by contact with cooled water, and isolated by standard techniques. Advantageously, the method can be

used to sulphonate 100 mole% of Ph² phenyl groups and once this level of sulphonation has been effected no further sulphonation occurs. Thus, there is no need to precisely control the sulphonation conditions (e.g. reaction time) beyond ensuring that the reaction has proceeded long enough to substantially fully mono-sulphonate the Ph² phenyl groups. This facilitates the preparation of batches of substantially identical ion-conductive polymeric materials and contrasts with processes which need to be stopped when a desired level of sulphonation has been achieved, for example where more vigorous conditions are used to sulphonate -O-phenyl-CO-groups in polymeric materials.

When said ion-conducting polymeric material includes a third unit which is amorphous and not provided with ion-exchange sites, the polycondensation reaction may be carried out in the presence of one or more other monomers. Preferred examples of such other monomers are Bis-S and 2,4-DHB. Other examples are 1,3-bis(4-fluorobenzoyl)benzene(1,3-DKDF) and its sulphone analogue.

Preferred combinations of monomers which after polycondensation and treatment to provide ion-exchange sites (e.g. after sulphonation) may be of utility in fuel cells as described are detailed in the Table below wherein the * in each row indicates the monomers which can be used to prepare preferred polymers. The following abbreviations are used in the table:

BDF	4,4'-difluorobenzophenone
HQ	hydroquinone
DHB	4,4'-dihydroxybenzophenone
Bis-S	4,4'-dihydroxydiphenylsulphone

DCDPS 4,4'-dichlorodiphenylsulphone
 DFDPS 4,4'-difluorodiphenylsulphone
 2,4-DHB 2,4-dihydroxybenzophenone
 1,3-DKDF 1,3-bis-(4-fluorobenzoyl)benzene

5

BDF	DHB	HQ	DCDPS/DFDPS	Bis-S	2,4-DHB	1,3-DKDF	Sulphone analogue of 1,4-DKDF	Sulphone analogue of 1,3-DKDF
*	*	*						
*	*	*		*				
*	*	*			*			
*	*	*				*		
*	*	*					*	
*	*	*						*
*	*	*	*					
*	*	*	*	*				
*	*	*	*		*			
*	*	*	*			*		
*	*	*	*				*	
*	*	*	*					*

According to a sixth aspect of the invention, there is provided a method of making a polymer electrolyte membrane of a fuel cell or electrolytic cell (especially of a fuel cell), the method including providing an ion-conductive polymeric material as described herein in solution, forming said solution into a desired form (e.g. casting the solution to form a membrane) and providing conditions for removal of the solvent of said solution.

15

According to a seventh aspect of the invention, there is provided a method of making a membrane electrode assembly of a fuel cell, the method comprising associating a catalyst material with an ion-conductive polymeric material as described herein.

20

Any feature of any aspect of any invention or embodiment described herein may be combined with any feature of any aspect of any other invention or embodiment
5 described herein mutatus mutandis.

Specific embodiments of the invention will now be described by way of example.

10 In the following examples, abbreviations used are as hereinbefore described.

The following products are referred to hereinafter:

15 PEEK™450P (Trade Mark) - polyetheretherketone obtained from Victrex Plc of Thornton Cleveleys, UK.
PEK™P22 (Trade Mark) - polyetherketone also obtained from Victrex Plc.

20 Unless otherwise stated, all chemicals referred to hereinafter were used as received from Sigma-Aldrich Chemical Company, Dorset, U.K. 1,3-DKDF can be made as described in Polymer 29, 358 (1988).

25 **Example 1a**

A 700ml flanged flask fitted with a ground glass Quickfit lid, stirrer/stirrer guide, nitrogen inlet and outlet was charged with 4,4'-difluorobenzophenone (88.85g,
30 0.4072 mole) (BDF), hydroquinone (24.22g, 0.22 mole) (HQ), 4,4'-dihydroxybenzophenone 38.56g, 0.18 mole) (DHB) and diphenylsulphone (320g) and purged with nitrogen for over 1 hour. The contents were then heated under a nitrogen

blanket to between 140 and 150°C to form an almost colourless solution. While maintaining a nitrogen blanket, dried sodium carbonate (42.39g, 0.4 mole) and potassium carbonate (1.10g, 0.008 mole) were added. The temperature
5 was raised gradually to 330°C over 3 hours then maintained for 20 minutes.

The reaction mixture was allowed to cool, milled and washed with acetone and water. The resulting polymer was
10 dried in an air oven at 120°C. The polymer had a melt viscosity at 400°C, 1000sec⁻¹ of 0.46 kNsm⁻².

Example 1b

15 A 700ml flanged flask fitted with a ground glass Quickfit lid, stirrer/stirrer guide, nitrogen inlet and outlet was charged with 4,4'-difluorobenzophenone (88.85g, 0.4072 mole), hydroquinone (24.22g, 0.22 mole), 4,4'-dihydroxybenzophenone (34.32g, 0.160 mole), 4,4'-
20 dihydroxydiphenylsulphone (5.0g, 0.02 mole), and diphenylsulphone (320g) and purged with nitrogen for over 1 hour. The contents were then heated under a nitrogen blanket to between 140 and 150°C to form an almost colourless solution. While maintaining a nitrogen blanket,
25 dried sodium carbonate (43.24g, 0.408 mole) was added. The temperature was raised gradually to 330°C over 3 hours then maintained for 50 minutes.

The reaction mixture was allowed to cool, milled and
30 washed with acetone and water. The resulting polymer was dried in an air oven at 120°C. The polymer had a melt viscosity at 400°C, 1000sec⁻¹ of 0.34 kNsm⁻².

Examples 1c - 1e

The polymerisation procedure of Example 1b was followed, for 1c - 1e, except that copolymer was prepared by varying the mole ratios of the hydroxy-containing reactants and by omission of the potassium carbonate.

A summary of the mole ratios and MVs are detailed in Table 1 below.

Table 1

Example	Polymer Composition (mole ratio)				MV (kNsm ⁻²)
	BDF	HQ	DHB	Bis-S	
1a	1.02	0.55	0.45	-	0.46
1b	1.02	0.55	0.40	0.05	0.34
1c	1.02	0.55	0.36	0.09	0.55
1d	1.02	0.58	0.42	-	0.32
1e	1.02	0.65	0.35	-	0.34

Examples 2a -2e Sulphonation of Polymers Examples 1a-1e

The polymers from Examples 1a - 1e were sulphonated by stirring the respective polymers in 98% sulphuric acid (7.0g polymer/100g sulphuric acid) for >21 hours at 65°C. Thereafter, the reaction solution was allowed to drip into stirred deionised water. Sulphonated polymer was precipitated as free-flowing beads. Recovery was by filtration, followed by washing with deionised water until the pH was neutral and subsequent drying. In general, titration confirmed that 100 mole% of the phenyl groups present as ether-phenyl-ether para linkages had sulphonated, giving one sulphonic acid group, ortho to the ether linkage, on each of the aromatic rings. The phenyl

groups present in ether-phenyl-ketone moieties were unsulphonated as were the phenyl groups present in ether-phenyl-ketone-phenyl-ether-sulphones moieties (if present).

5

Examples 2f - Sulphonation of polyetheretherketone (comparative)

10 A 500ml, 3-necked, round-bottomed flask fitted with a stirrer/stirrer guide, nitrogen inlet and outlet and a thermometer was charged with 98% sulphuric acid (180g). The sulphuric acid was heated under a blanket of nitrogen to 50°C. While maintaining a nitrogen blanket and stirring polyetheretherketone (PEEK™ 450P, Victrex plc) was added.
15 The polymer dissolved and was stirred at 50°C for 90 minutes. The solution was quickly cooled to 20°C, thereafter allowed to drip into stirred deionised water. Sulphonated polymer precipitated as free-flowing beads. Recovery was by filtration, followed by washing with
20 deionised water until the pH was neutral and subsequent drying. By titration the Equivalent Weight was 644. It should be appreciated that the EW depends on the duration and temperature of the sulphonation reaction - the greater the duration and temperature, the more sulphonated the
25 polymer.

Examples 2g - Sulphonation of polyetherketone (comparative)

30 A 500ml, 3-necked, round-bottomed flask fitted with a stirrer/stirrer guide, nitrogen inlet and outlet and a thermometer was charged with 98% sulphuric acid (180g) and, while stirring, polyetherketone (PEK™ P22, Victrex

plc) (20g) was added. The temperature was increased to 55°C and oleum (20% free SO₃) (120g) was added. The solution was stirred for 60 minutes at 35°C. The solution was quickly cooled to 20°C, thereafter, allowed to drip into stirred
5 deionised water. Sulphonated polymer precipitated as free-flowing beads. Recovery was by filtration, followed by washing with deionised water until the pH was neutral and subsequent drying. By titration the Equivalent Weight was 667. As for Example 2f, the greater the duration and
10 temperature of the sulphonation reaction, the more sulphonated the polymer.

Examples 3a-3g - Membrane Fabrication

15 Membranes were produced from the sulphonated polymers of respective Examples 2a-2g by dissolving respective polymers in N-methylpyrrolidone (NMP). The polymers were dissolved at 80°C at their maximum concentration. The homogeneous solutions were cast onto clean glass plates
20 and then drawn down to give 400 micron films, using a stainless steel Gardner Knife. Evaporation at 100°C under vacuum for 24 hours produced membranes of mean thickness 40 microns.

25 Examples 4a- 4g Water-uptake of the Membranes

5cm x 5cm x 40 microns sample of the membranes from Examples 3a-3g were immersed in boiling deionised water (500ml) for 60 mins, removed and dried quickly with lint-free paper to remove surface water, weighed, dried in an
30 oven at 50°C for 1 day, allowed to cool to ambient temperature in a desiccator then weighed quickly. The %

water-uptake was calculated as follows and the results are provided in Table 2.

$$\% \text{ Water-uptake} = \frac{\text{Wet Weight} - \text{Dry Weight}}{\text{Dry Weight}} \times 100$$

Table 2

Sulphonated polymer from Example No.	Boiling water uptake as described in Example 4 (%)	Theoretical EW	Actual EW (by titration)
3a	59	690	700
3b	93	692	667
3c	135	695	733
3d	106	645	641
3e	234	579	590
3f (comp)	Broke up	-	644
3g (comp)	370	-	670

10

Referring to Table 2, it should be noted that the sulphonated polyetherketone polymer (Example 3g) had a substantially higher boiling water uptake compared to the copolymers of Examples 3a to 3e for comparable EW. In the case of sulphonated polyetheretherketone (Example 3f) the boiling water uptake was so high that the polymeric material broke up. It is highly surprising that whereas respective homopolymers of sulponated polyetheretherketone and sulphonated polyetherketone have very high boiling water uptakes, copolymers comprising sulphonated polyetheretherketone with polyetherketone have significantly lower boiling water uptakes for similar EWs.

Example 5 - Post treatment of the Membranes of Examples 4a, 4c and 4e with acetone

5 The 5cm x 5cm x 40 microns sample of membrane from Examples 4a, 4c and 4e were immersed in refluxing acetone (100ml) for 60 mins, removed and dried in an oven at 50°C for 1 day, immersed in boiling deionised water (500ml) for 60 mins, removed and dried quickly with lint-free paper to
10 remove surface water, weighed, dried in an oven at 50°C for 1 day, allowed to cool to ambient temperature in a desiccator then weighed quickly. The % water-uptake was calculated as described previously and summarised in Table 3.

15

Table 3

Sulphonated polymer from Example No.	Boiling water uptake as described in Example 4 (%)	Boiling water uptake after acetone treatment as described in Example 5 (%)
3a	59	61
3c	135	84
3e	234	100

20 The acetone treatment can increase crystallinity of crystalline polyaryletherketones. Table 3 shows that a substantial reduction in boiling water uptake can be achieved in some circumstances (Examples 3c and 3e). In some cases, where crystallinity of the polymer is already high, the acetone treatment cannot effect an increase
25 (Example 3a).

The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and
5 which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

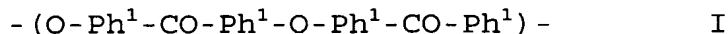
All of the features disclosed in this specification
10 (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

15 Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly
20 stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

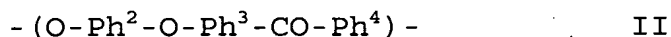
The invention is not restricted to the details of the
25 foregoing embodiment(s). The invention extend to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so
30 disclosed.

CLAIMS

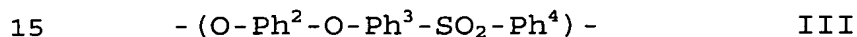
1. A fuel cell or an electrolytic cell comprising an ion-conductive polymeric material which includes a first
5 repeat unit of formula



and a second repeat unit of formula
10



or of formula



wherein Ph^1 , Ph^2 , Ph^3 and Ph^4 independently represent phenyl moieties and wherein said second repeat unit is provided with ion-exchange sites.
20

2. A cell according to claim 1, wherein said ion-conductive polymeric material is crystalline.

3. A cell according to claim 1 or claim 2, wherein said
25 ion-conductive polymeric material includes a repeat unit which is crystalline and a repeat unit which is amorphous.

4. A cell according to any preceding claim, wherein said first repeat unit is crystalline.

30 5. A cell according to any preceding claim, wherein said first repeat unit comprises unsubstituted phenyl groups

Ph¹ with said groups Ph¹ having 1,4-linkages to the -O- and -CO- groups to which they are bonded.

6. A cell according to any preceding claim, wherein said
5 second repeat unit includes ion-exchange sites.

7. A cell according to any preceding claim, wherein said second repeat unit is sulphonated.

10 8. A cell according to any preceding claim, wherein Ph³ represents an unsubstituted phenyl group having 1,4-linkages to the -O- and -CO- or -SO₂- groups to which it is bonded.

15 9. A cell according to any preceding claim, wherein Ph⁴ represents an unsubstituted phenyl group having 1,4-linkages to the -O- and -CO- or -SO₂- groups to which it is bonded.

20 10. A cell according to any preceding claim, wherein Ph² represents a phenyl group provided with an ion-exchange site wherein the phenyl group has 1,4-linkages to the -O- groups to which it is bonded.

25 11. A cell according to any preceding claim, wherein less than 1 mole% of groups Ph¹ in said polymeric material are functionalised; less than 1 mole % of groups Ph³ in said second unit are functionalised; less than 1 mole% of groups Ph⁴ are functionalised; and greater than 70 mole%
30 of groups Ph² in said second unit are provided with ion-exchange sites.

12. A cell according to any preceding claim, wherein said second repeat unit is an -ether-(monosulphonated)phenyl-ether-(unsubstituted)phenyl-carbonyl-unsubstituted)phenyl-unit.

5

13. A cell according to any preceding claim, wherein "a" represents the mole% of units of formula I in said ion-conductive polymeric material and "b" represents the sum of the mole% of units of formula II and III in said polymeric material, wherein the ratio of "a" to "b" in
10 said polymeric material is less than 4 but is at least 0.15.

14. A cell according to any preceding claim, wherein said
15 ion-conductive polymeric material includes a third repeat unit which is different from units I, II and III, wherein said third unit is amorphous.

15. A cell according to claim 14 which includes at least
20 one of the following: a sulphone moiety in the polymer backbone; a 1,3-disubstituted phenyl moiety in the polymer backbone; or a functional group pendent from a phenyl moiety in the polymer backbone.

25 16. A cell according to any preceding claim, wherein the equivalent weight (EW) of said ion-conductive polymeric material is less than 850 g/mol and is greater than 300 g/mol.

30 17. A polymer electrolyte membrane for a fuel cell or electrolytic cell, the membrane comprising an ion-conductive polymeric material according to any of claims 1 to 16.

18. A membrane electrode assembly for a fuel cell which comprises an ion-conductive polymeric material as described in any of claims 1 to 16 associated with a catalyst material.

5

19. A method of making a fuel cell or electrolytic cell, the method comprising incorporating an ion-conductive polymeric material as described in any of claims 1 to 16 into said fuel cell or electrolytic cell.

10

20. A method of making a fuel cell or electrolytic cell, the method comprising incorporating, into the fuel cell or electrolytic cell, an ion-conductive polymeric material prepared by:

15

(A) polycondensing 4,4'-dihydroxybenzophenone (DHB), 4,4'-difluorobenzophenone (BDF) and hydroquinone (HQ);

(B) treating the polymeric material formed with a means
20 for providing said ion-exchange sites.

21. A method according to claim 20, wherein said means for providing said ion-exchange sites involves sulphonating the polymeric material.

25

1/1

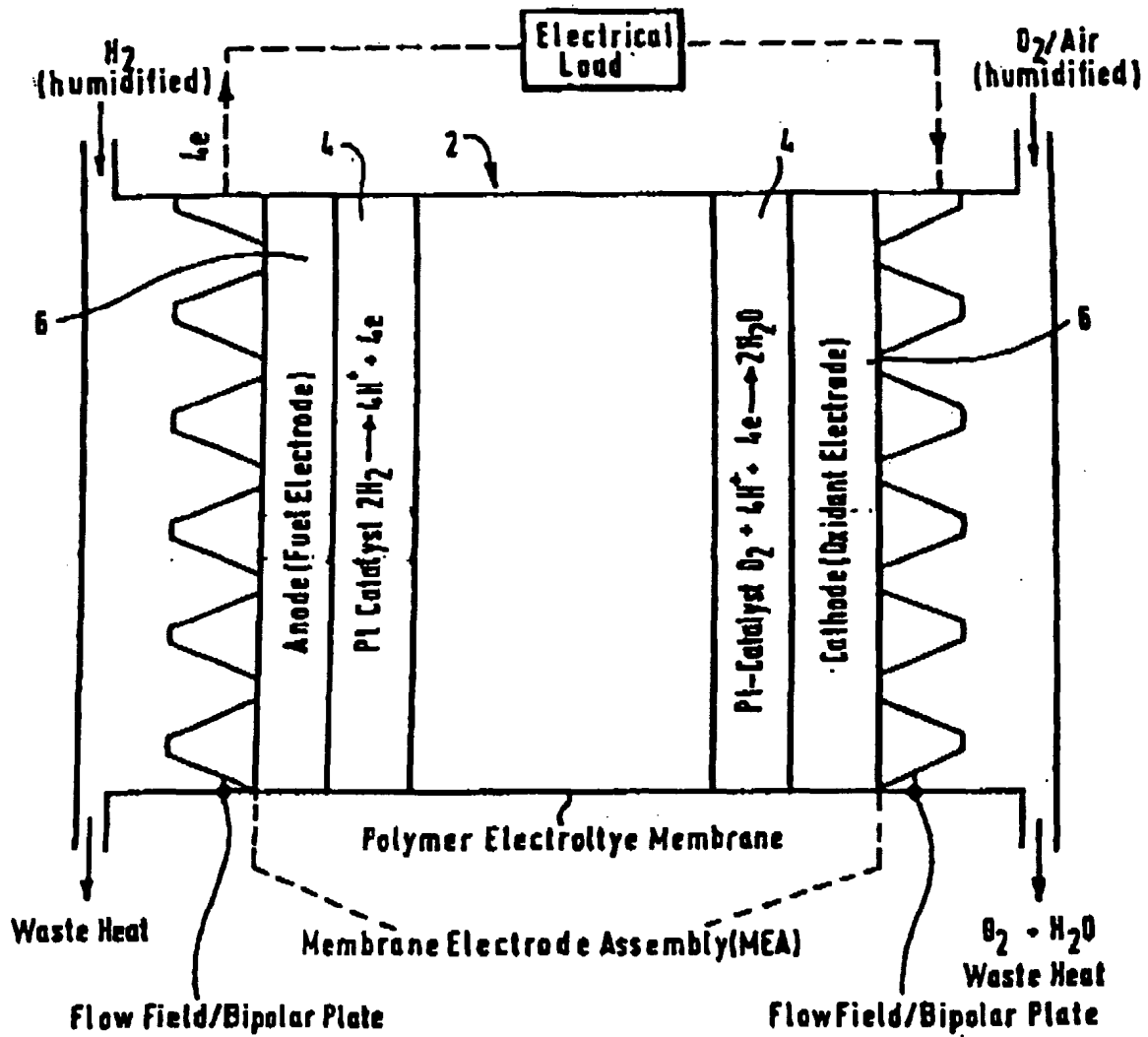


Figure 1

DERWENT-ACC-NO: 2003-468154**DERWENT-WEEK:** 201062*COPYRIGHT 2010 DERWENT INFORMATION LTD*

TITLE: Fuel cell or electrolytic cell comprises ion-conductive polymeric material which includes two repeat units comprising phenyl moieties

INVENTOR: DEVINE J N; WILSON B

PATENT-ASSIGNEE: DEVINE J N[DEVII] , VICTREX MFG LTD
[VICTN] , WILSON B[WILSI]

PRIORITY-DATA: 2001GB-023109 (September 26, 2001)**PATENT-FAMILY:**

PUB-NO	PUB-DATE	LANGUAGE
WO 03028139 A2	April 3, 2003	EN
EP 1430559 A2	June 23, 2004	EN
AU 2002329405 A1	April 7, 2003	EN
US 20040258999 A1	December 23, 2004	EN
JP 2005504421 W	February 10, 2005	JA
EP 1430559 B1	May 30, 2007	EN
DE 60220425 E	July 12, 2007	DE
DE 60220425 T2	January 31, 2008	DE
AU 2002329405 B2	May 1, 2008	EN
US 7799465 B2	September 21, 2010	EN

DESIGNATED-STATES: AE AG AL AM AT AU AZ BA BB BG BR BY
 BZ CA CH CN CO CR CU CZ DE DK DM DZ
 EC EE ES FI GB GD GE GH GM HR HU ID IL
 IN IS JP KE KG KP KR KZ LC LK LR LS LT
 LU LV MA MD MG MK MN MW MX MZ NO
 NZ OM PH PL PT RO RU SD SE S G SI SK SL
 TJ TM TN TR TT TZ UA UG US UZ VC VN YU
 ZA ZM ZW AT BE BG CH CY CZ DE DK EA
 EE ES FI FR GB GH GM GR IE IT KE LS LU
 MC MW MZ NL OA PT SD SE SK SL SZ TR
 TZ UG ZM ZW AL AT BE BG CH CY CZ DE
 DK EE ES FI FR GB GR IE IT LI LT LU LV MC
 MK NL PT RO SE S I SK TR AT BE BG CH CY
 CZ DE DK EE ES FI FR GB GR IE IT LI LU MC
 NL PT SE SK TR

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
WO2003028139A2	N/A	2002WO-GB04242	September 18, 2002
AU2002329405A1	N/A	2002AU-329405	September 18, 2002
AU2002329405B2	N/A	2002AU-329405	September 18, 2002
DE 60220425E	N/A	2002DE-620425	September 18, 2002
DE 60220425T2	N/A	2002DE-620425	September 18, 2002
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EP 1430559B1	N/A	2002EP-765031	September 18, 2002
EP 1430559A2	PCT Application	2002WO-GB04242	September 18, 2002
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JP2005504421W	PCT Application	2002WO-GB04242	September 18, 2002
EP 1430559B1	PCT Application	2002WO-GB04242	September 18, 2002
DE 60220425E	PCT Application	2002WO-GB04242	September 18, 2002
DE 60220425T2	PCT Application	2002WO-GB04242	September 18, 2002
US 7799465B2	PCT Application	2002WO-GB04242	September 18, 2002
JP2005504421W	N/A	2003JP-531548	September 18, 2002
US20040258999A1	N/A	2004US-490422	April 28, 2004
US 7799465B2	Based on	2004US-490422	April 28, 2004

INT-CL-CURRENT:

TYPE	IPC DATE
CIPP	C08J5/22 20060101
CIPP	C08J5/22 20060101
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CIPS	C08G65/40 20060101
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CIPS	C08J5/22 20060101

CIPS	C08J5/22 20060101
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ABSTRACTED-PUB-NO: WO 03028139 A2

BASIC-ABSTRACT:

NOVELTY - Fuel cell or electrolytic cell comprises an ion-conductive polymeric material which includes first and second repeat units comprising phenyl moieties. The second repeat unit is provided with ion-exchange sites.

DESCRIPTION - Fuel cell or electrolytic cell comprises an ion-conductive polymeric material which includes a first repeat unit of formula $-(O-Ph-CO-Ph-O-Ph-CO-Ph)-$ (I) and a second repeat unit of formula $-(O-Ph_2-O-Ph_3-CO-Ph_4)$ (II) or $-(O-Ph_2-O-Ph_3-SO_2-Ph_4)-$ (III). The second repeat unit is provided with ion-exchange sites.

Ph, Ph₂, Ph₃, and Ph₄ = phenyl moieties.

INDEPENDENT CLAIMS are also included for:

(a) a polymer electrolyte membrane or a membrane electrode assembly for a fuel cell or electrolytic cell, which comprises an ion-conductive polymeric material associated with a catalyst material; and

(b) a method of making a fuel cell or electrolytic cell, which comprises incorporating an ion-conducting polymeric material into the fuel cell or electrolytic cell.

USE - Used as a fuel cell or electrolytic cell.

ADVANTAGE - The ion-conductive polymeric material has boiling water uptakes which, when used in fuel cells and/or electrolytic cells, are much lower than expected.

EQUIVALENT-ABSTRACTS:

POLYMERS

Preferred Components: The ion-conductive polymeric material is crystalline. It includes a repeat unit which is crystalline and a repeat unit which is amorphous. The first repeat unit is crystalline and comprises unsubstituted phenyl groups, Ph1, having 1,4-linkages to the -O- and -CO- groups to which they are bonded. The second repeat unit includes ion-exchange sites or is sulfonated. Less than 1 mole% of groups Ph1 in the polymeric material are functionalized, less than 1 mole% of groups Ph3 in the second unit are functionalized, less than 1 mole% of groups Ph4 are functionalized, and greater than 70 mole% of groups Ph2 in the second unit are provided with ion-exchange sites.

The second repeat unit is an -ether-(monosulfonated)phenyl-ether-(unsubstituted)

phenyl-carbonyl-unsubstituted)phenyl-unit. The ratio of the mole% of units of formula (I) to the sum of the mole% of units of formulae (II) and (III) in the polymeric material is less than 4 but is at least 0.15.

The polymeric material includes an amorphous third repeat unit which is different from units (I), (II), and (III). The cell includes a sulfone moiety in the polymer backbone, a 1,3-disubstituted phenyl moiety in the polymer backbone, and/or a functional group pendent from a phenyl moiety in the polymer

backbone. The equivalent weight (EW) of the ion-conductive polymeric material is less than 850 g/mol and is greater than 300 g/mol.

Preferred Method: The ion-conductive polymer is prepared by polycondensing 4,4'-dihydroxybenzophenone (DHB), 4,4'-difluorobenzophenone (BDF) and hydroquinone (HQ). The ion-exchange sites are provided by sulfonating the polymeric material.

Preferred Definitions:

Ph3, Ph4 = unsubstituted phenyl group having 1,4-linkages to the -O- and -CO- or -SO2- groups to which it is bonded; and

Ph2 = phenyl group provided with an ion-exchange site and having 1,4-linkages to the -O- groups to which it is bonded.

A flask with a stirrer, nitrogen inlet and outlet was charged with BDF (88.85 g), HQ (24.22 g), DHB (38.56 g) and diphenylsulfone (320 g) and purged with nitrogen for over 1 hour. The contents were heated under a nitrogen blanket to 140-150 degrees C to form an almost colorless solution. While maintaining a nitrogen blanket, dried sodium carbonate (42.39 g) and potassium carbonate (1.1 g) were added. The temperature was raised gradually to 330 degrees C over 3 hours and maintained for 20 minutes. The reaction mixture was allowed to cool, milled, and washed with acetone and water. The resulting polymer was dried in an air oven at 120 degrees C. The polymer had a melt viscosity at 400 degrees C, 1000/sec of 0.46 kNsm⁻².

The polymer (7.0 g) was sulfonated with 98 % sulfuric acid (100 g) by stirring at 65 degrees C for over 21 hours. The reaction mixture was allowed to drip into stirred deionized water to precipitate polymer as free flowing beads. The beads were filtered off, washed with deionized water until the pH was neutral and dried. Titration confirmed 100 mole% of the phenyl groups present as ether-phenyl-ether para linkages were sulfonated, giving one sulfonic acid group ortho to the ether linkage on each aromatic ring. Phenyl groups present in ether-phenyl-ketone moieties were unsulfonated as were those in ether-phenyl-ketone-ether-sulphones moieties if present.

The polymer was made into a membrane by dissolving it in N-methylpyrrolidone at 80 degrees C at the maximum concentration. The solution

was cast into a glass plate then drawn down to give a 400 micrometers film using a Gardner knife. Evaporation at 100 degrees C under vacuum for 24 hours produced membranes of mean thickness of 40 micrometers.

Water uptake by the polymer membrane was measured by immersing a 5 cm x 5 cm film in boiling water (500 g) for 1 hour, surface dried and weighed, than dried at 50 degrees C for 1 day, cooled and re weighed. The % water uptake (weight difference dry and wet/dry weight) was 59 %. The theoretical equivalent weight was 690. The actual equivalent weight by titration was 700.

Comparative examples using polyetheretherketone and polyetherketone broke up on the water uptake test or gave 370 %, respectively.

TITLE-TERMS: FUEL CELL ELECTROLYTIC COMPRISE ION
CONDUCTING POLYMERISE MATERIAL TWO
REPEAT UNIT PHENYL MOIETY

DERWENT-CLASS: A28 A85 L03 X16

CPI-CODES: A05-H07A; A12-E06A; A12-E06B; L03-E04A2;

EPI-CODES: X16-C01C; X16-J01A;

ENHANCED-POLYMER-INDEXING: Polymer Index [1.1] 018 ; G1194
G1150 G1149 G1092 D01 D19
D18 D32 D76 F23 F32 F30; G1149
G1092 D01 D19 D18 D31 D50
D76 D86 F32 F30 R01041 58;
G1978 D01 D19 D18 D32 D50
D69 D76 D93 F23 F* 7A R24002
53532; P0964*R F34 D01; H0033
H0011; M9999 M2799; L9999
L2528 L2506; L9999 L2200;
L9999 L2799; L9999 L2391;
L9999 L2664 L2506;

Polymer Index [1.2] 018 ; D01 D19
D18 D11 D10 D33 D34 D76 D50
D93 D94 F23 F34 F61; P1149*R

F23 D01; P0964*R F34 D01;
P1490*R F61 D01; H0260; L9999
L2528 L2506; L9999 L2799;
L9999 L2200; L9999 L2391;
L9999 L2664 L2506; M9999
M2799;

Polymer Index [1.3] 018 ; ND04;
ND01; Q9999 Q7410 Q7330;
Q9999 Q7396 Q7330; Q9999
Q7772; B9999 B3269 B3190;
Q9999 Q7409 Q7330; Q9999
Q8060; B9999 B4795 B4773
B4740; B9999 B4784 B4773
B4740; N9999 N6155; B9999
B3612 B3554; N9999 N6848
N6655; N9999 N6780*R N6655;
N9999 N6882 N6655; N9999
N6804*R N6655; N9999 N5890
N5889; N9999 N5743; N9999
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B9999 B3407 B3383 B3372;

Polymer Index [1.4] 018 ; S* 6A;
H0157;

Polymer Index [1.5] 018 ; D00 D60
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Polymer Index [1.6] 018 ; D00 F44
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107324; D00 F44 C* 4A O* 6A K*
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C999 C306; C999 C340;

Polymer Index [1.7] 018 ; D01 D19
D18 D32 D50 D76 D92 F61
R06943 2107; A999 A475;

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